Unsymmetrical Biaryls from Dialkylacetylenes and Aryl Iodides in the Presence of Nickel Halides and Zinc Metal

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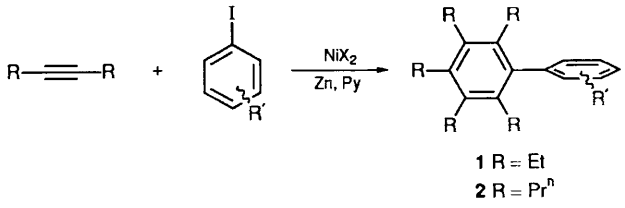
Dialkylacetylenes RC≡CR (R = Et or Pr^n) react with aryl iodides in the presence of nickel halides, zinc powder and pyridine to give unsymmetrical biaryls **1** and **2** in moderate yields.

It is known that nickel complexes in the presence of reducing agents react with aryl halides to give symmetrical biaryls[1] and also may be employed as catalysts for the coupling of aryl halides with aryl organometallics yielding unsymmetrical biaryls.[2] In addition, they are effective catalysts for the trimerization of acetylenes.[3] In this report, we describe an interesting new synthesis of unsymmetrical biaryls from the reaction of dialkylacetylenes with aryl iodides in the presence of nickel halides and zinc powder (Scheme 1). This reaction involves the cleavage of a carbon–carbon bond and the



1 R = Et
2 R = Pr^n

Scheme 1

Table 1 Formation of biaryls from aryl iodides and dialkylacetylenes[a]

Product	Aryl iodide	Catalyst	Yield (%)[b]
1a	*p*-$MeOC_6H_4I$	NiI_2	39
1b	*p*-ClC_6H_4I	$NiBr_2$	50
1c	*p*-IC_6H_4I	NiI_2	17
1d	*p*-MeC_6H_4I	$NiBr_2$	27
1e	PhI	$NiBr_2$	29
1f	*m*-$MeOC_6H_4I$	$NiBr_2$	15
1g	*m*-BrC_6H_4I	NiI_2	40
1h	*m*-ClC_6H_4I	NiI_2	14
2a	*p*-$MeOC_6H_4I$	NiI_2	24
2b	*p*-ClC_6H_4I	NiI_2	38

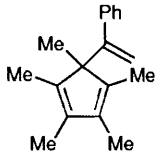
[a] All reactions were carried out under the following conditions and stoichiometry: NiX_2, 0.36 mmole; Zn, 1.8 mmole; dialkylacetylene (**1a–1h**: hex-3-yne, **2a**, **2b**: oct-4-yne), 3.6 mmole; aryl iodide, 1.2 mmole; pyridine, 0.2 mmole at 60 °C for 24 h. [b] Yields are not optimized, are based on the starting aryl iodides and are given for pure, isolated products.

formation of four new carbon–carbon bonds. Moreover it appears to result from a combination of acetylene trimerization and aryl coupling mediated by the nickel complex.

In general, the reaction solutions were prepared by mixing the dialkylacetylene, pyridine, aryl iodide, nickel halide and zinc powder in acetonitrile under nitrogen. The solutions were heated with stirring at 60°C for *ca.* 24 h. Separation of the mixtures on silica gel using hexane–ethyl acetate–methylene chloride as the eluent gave the desired products. The detailed conditions and the yields are summarized in Table 1.

The assignment of structures **1a–1h**, **2a** and **2b** is mainly based on their NMR and mass spectral data. Taking **1a** as an example, there are three ethyl groups at δ 0.91, 2.31; 1.21, 2.68; 1.25, 2.72 with a 2:2:1 intensity ratio, two aromatic proton signals at δ 6.92 (d) and 7.13 (d) and a methyl signal at δ 3.86 (s) in the ^1H NMR spectrum. These spectral data are fully in agreement with the structure assigned for **1a**. An upfield shift for the resonances of the *ortho* ethyl protons relative to the *meta* and *para* ones is observed. Presumably, this results from the fact that the two aromatic rings in **1a** are nearly perpendicular leading to a ring-current on the *ortho* substituents. As expected, the ^{13}C NMR spectrum of **1a** exhibits six quaternary carbon signals [δ 113.11 (d), 131.14 (d), 134.71 (s), 137.66 (s), 138.80 (s), 139.67 (s), 139.93 (s) and 158.21 (s)] in the aromatic region and one methyl signal for the methoxy group [δ 55.08 (q)]. However, there are only two sets of ethyl resonances [δ 15.64 (q), 21.99 (t); 15.49 (q), 23.35 (t)] in a 3:2 intensity ratio instead of the required three sets indicating that the ethyl groups at the *para* and *meta* positions have the same ^{13}C chemical shift. The high resolution mass spectrum of **1a** also agrees with the proposed structure.

A comparison of the products and the reactants in Scheme 1 indicates that one of the carbon–carbon bonds between the substituent R and the acetylene group is cleaved during the course of the reaction. Analysis of the gas mixtures above the reaction solutions by mass spectrometry reveals that the Et group in hex-3-yne and the Pr^n group in oct-4-yne are transformed into ethene and propene, respectively.



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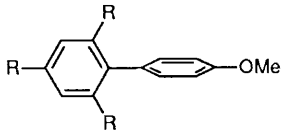
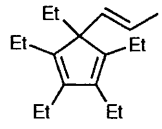


4a R = Bu^t
4b R = Bu^n



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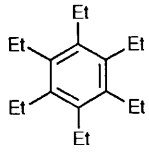

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As indicated in Table 1, most *para*- and *meta*-substituted aryl iodides are able to react with hex-3-yne or oct-4-yne to yield the unsymmetrical biaryls. However, there is no similar biaryl detected from the reaction of hex-3-yne and *ortho*-substituted aryl iodides presumably because of the large steric effect due to the *ortho*-substituent. The alkynes that are able to form compound **1** are limited. In addition to hex-3-yne and oct-4-yne, hex-2-yne also reacts with aryl iodides to give unsymmetrical biaryls but in several isomeric forms. Surprisingly, but-2-yne does not react with aryl iodides under the same conditions to yield the expected product but instead gave **3** as the major product.[4] Thus, it appears that the formation of the alkene, *e.g.* ethene and propene, from the alkyne is important for the reaction to proceed. The reaction of terminal alkynes such as *tert*-butylacetylene and hex-1-yne with iodoanisole under the same conditions led to the formation of **4** in low yield.

Under the conditions in Scheme 1 and using hex-3-yne as a reagent, compounds **5** and **6** were also observed in variable yield. These two species have been observed previously in the trimerization of alkynes by Ni or Pd complexes.[5] Neither **5** nor **6** reacts further with aryl iodides to give **1** indicating that they are not intermediates for the formation of **1**. At present, it is not clear how the unsymmetrical biaryls are produced, but attempts to understand the mechanism by isolating the reaction intermediates are in progress.

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